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Spectral studies and thermal analysis of new vanadium complexes of ethanolamine and related compounds

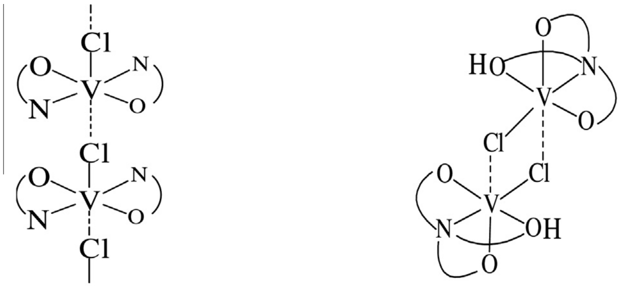
Mamdouh S. Masoud [a], Alaa E. Ali [b], Hytham M. Ahmed [c,*], Essam A. Mohamed [b]

[a] Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[b] Chemistry Department, Faculty of Science, Damanhour University, Damanhour, Egypt
[c] Pharmaceutical Analysis Department, Faculty of Pharmacy, Damanhour University, Damanhour, Egypt

HIGHLIGHTS

- Newly synthesized complexes of V^{III}, V^{IV} and VO^{2+} with ethanolamines were described.
- The complexes have been characterized by elemental analyses, magnetic moment measurements, IR and UV–Vis spectroscopy.
- Absorption spectra in seven different solvents were recorded.
- The solvatochromism was examined and discussed.
- Some complexes were studied by thermal analysis using DTA and TG techniques.

GRAPHICAL ABSTRACT



V^{III}- MEA and V^{III}- DEA complexes

V^{III} – TEA complex

The general formula of V^{III}- studied complexes.

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ABSTRACT

The electronic absorption spectral behaviors of newly synthesized complexes of V^{III}, V^{IV} and VO^{2+} with Ethanolamine, Diethanolamine and Triethanolamine were described. The complexes have been characterized by elemental analyses, magnetic moment measurements, IR and UV–Vis spectroscopy. Absorption spectra in seven different solvents were recorded. The solvatochromism was examined and discussed. Dipolar interactions between the solvent and the complexes were used to correlate the observed spectral shifts to solvent polarity. Some of the obtained complexes were studied by thermal analysis using DTA and TG techniques.

1. Introduction

Vanadium is an early first-row transition metal and forms colored compounds in its many different oxidation states depending on the electronic and steric nature of the coordinating ligands. In higher oxidation states, vanadium is very oxophilic, but at low oxidation states, π-donating ligands such as dinitrogen and carbon monoxide are preferred. Vanadium is a micronutrient element which has been shown to produce several important biological effects in living organisms [1–4]. Its deficiency causes growth retardation and skeletal deformations in animals. The catalytic and material properties of vanadium compounds and their effects in biological systems have long provided the impetus to studies of vanadium science [1,5–10]. Also, the effect of vanadium on living organisms was studied [11–13] and vanadium complexes and polyoxovanadate recently proved to be used as anticancer [14–19]. The bifunctional nature of the examined compounds enables

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* Corresponding author.
E-mail address: hmaahmed@yahoo.co.uk (H.M. Ahmed).

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them to serve a variety of commercial applications such as corrosion inhibitors, surfactants, gas purification, and herbicides and in the manufacture of cosmetics and pharmaceuticals [20]. They can also act as multidentate ligands through amino, hydroxyl, and deprotonated hydroxyl groups. Metal with the tested ligands complexes have been the subject of many studies arising mainly from their technical applications [21–23]. As a part of our ongoing research on the synthesis, spectral, thermal and structural analysis of Ethanolamine (MEA), Diethanolamine (DEA) and Triethanolamine (TEA) complexes with most classes of metals [24–33]. This paper explores the physicochemical properties of complexes derived from vanadium of different oxidation states with MEA, DEA and TEA.

2. Materials and methods

All chemicals were of analytical grade and used without further purification. The solutions were prepared in inert atmosphere (bubbling nitrogen) using double distilled water. The VCl_3 solutions were prepared immediately before each addition. The molar percentage of VO^{2+} in each solution was adjusted by direct titration with standard $KMnO_4$ solution to be less than 1%. The chemical structure, abbreviation and symbol for the three tested compounds are shown in Fig. 1.

2.1. Preparation of the complexes

2.1.1. Synthesis of V^{III} complexes

Anhydrous VCl_3 (6.4 mmol) was dissolved in 10 ml hot N,N-dimethylformamide (DMF) under a stream of nitrogen, then (12.8 mmol) of the tested ligand was added to the solution. The mixture was kept at 70 °C for 0.5 h with stirring. Dark greenish blue microcrystals of the produced complexes were observed. The complexes were filtered off, washed with dry diethyl ether and finally dried in a desiccator over anhydrous $CaCl_2$. The complexes were insoluble in organic solvents but soluble in hot water. Therefore the stock solutions were prepared in hot water and then 0.5 ml of the obtained solution was mixed with the used organic solvent.

2.1.2. Synthesis of V^{IV} complexes

Rather than using VCl_4 which is a convenient starting material due to its volatility and oxidative nature, it is preferred to use VCl_3. The complexes were prepared by addition of VCl_3 (0.01 mol) in 25 ml ethanol to a hot ethanol solution of the desired investigated ligand (0.02 mol). The reaction mixtures were refluxed with stirring for 2 h. Hot solutions were cooled to room temperature and green microcrystalline complexes were formed. The complexes were filtered, washed with cold ethanol and finally dried in a vacuum desiccator over anhydrous $CaCl_2$.

2.1.3. Synthesis of VO^{2+} complexes

The VO^{2+} complexes were prepared by two techniques:

By refluxing solutions of 0.01 mol of $VOCl_2$ in 30 ml of 50% methanol–water with 0.01 or 0.02 mol of tested compounds on hot plate equipped with a magnetic stirrer. The complexes precipitated from the boiling solutions and then filtered off under suction. The obtained crystals were washed well with 50% methanol–water solution and then dried in a vacuum desiccator over anhydrous $CaCl_2$.

$$VOCl_2 + HL \rightarrow VOLCl + HCl \quad VOCl_2 + 2HL \rightarrow VOL_2 + 2HCl$$

By dropwise addition of 0.1 mol $VOSO_4$ solution in 30% methanol–water solution to 0.01 or 0.02 mol of the desired ligand solution in methanol–water solution. The complexes were separated immediately, washed, filtered then dried in a vacuum desiccator over anhydrous $CaCl_2$.

$$VOSO_4 + 2HL \rightarrow VOL_2 + H_2SO_4$$

2.2. Elemental analysis

2.2.1. Metal ion content

The complexes were digested and decomposed with aquaregia. The metal ion contents were determined by the usual complexmetric titration procedures [34] and atomic absorption technique.

2.2.2. Halogen and sulphate contents

The halogen content was determined by burning 30 mg of the sample in an oxygen flask in the presence of $KOH–H_2O_2$ mixture and titrating with a standard $Hg(NO_3)_2$ solution using diphenyl carbazone as an indicator [35]. The sulphate content was determined gravimetrically as $BaSO_4$ [35] and found to be zero in all complexes.

2.3. Physical measurements

2.3.1. Electronic absorption spectra

Ultraviolet and visible spectra were recorded using Perkin Elmer spectrophotometer model Lambda 4B covering the wavelength range 190–900 nm. The complexes were measured in Nujol mull, following the method described by Lee et al. [36].

2.3.2. Infrared spectra

The IR spectra were recorded using Perkin Elmer spectrophotometer model 1430 covering the frequency range of 200–

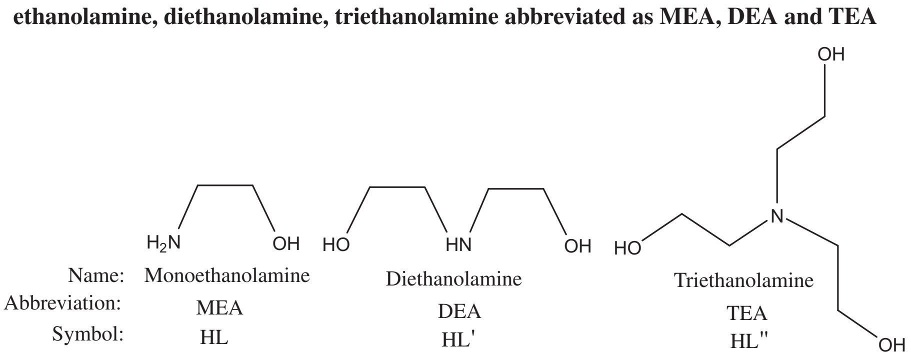

Fig. 1. The chemical structure, abbreviation and symbol for investigated compounds.